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The Effects of Highly Structured Low Density Carbon Nanotube Networks on the Thermal Degradation Behaviour of Polysiloxanes

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polymer degradation and stability

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Abstract: Carbon aerogel-carbon nanotube (CNT-CA) nanofoam networks are a member of a novel class of ultra-low density, high surface area, hierarchically structured inorganic carbon based materials possessing unique mechanical and physical properties. Through the secondary incorporation of a polymer matrix into these aerogel systems it is now possible to form intercalated polymeric hybrid CNT-CA composite materials with polymer to carbon surface internal surface contact areas in the order of $\sim 200\text{m}^2\text{g}^{-1}$ at carbon loadings as low as $\sim 1.5\text{ wt \%}$. Reported here is the synthesis of a series of well-defined poly(dimethylsiloxane) (PDMS)-CNT-CA composite systems, their characterization and the in-depth analysis of the effects of the carbon architecture on the thermal stability and degradation behaviour of the of the PDMS matrix. The results of degradative thermal analysis using both pyrolysis gas-chromatography/mass spectrometry (py-GC/MS) and thermogravimetric analysis (TA), clearly demonstrate that the presence of the CNT-CA scaffold within the PDMS matrix greatly increases the thermal stability of the system and drives the matrix towards calcination at temperatures above 600°C . Subsequent characterization of the residual materials using a combination of fast magic angle spinning solid-state nuclear magnetic resonance (Fast-MAS NMR), energy dispersive X-ray spectroscopy (EDAX) and electron microscopy have demonstrated that the improvements in thermal stability are concurrent with the relative loading of carbon nanotubes within the aerogel matrix, that the PDMS matrix is being driven towards the formation of increased levels of SiO_2 on degradation and that the preferential calcination effect is a function of the unique high surface area fibular network structure of the CNT-CA monoliths.

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Dear Sir,

Please find for your consideration, our manuscript titled “The Effects of Highly Structured Low Density Carbon Nanotube Networks on the Thermal Degradation Behaviour of Polysiloxanes”. In this work, we report the synthesis of a highly novel series of PDMS/carbon nanotube ‘foam’ physical composite systems and an in-depth study of their degradation behavior. Our results clearly demonstrate that the inclusion of an ultra-low density CA-CNT inorganic carbon framework into a crosslinked poly(dimethylsiloxane) network has a significant effect on the non-oxidative thermal stability and condensed phase degradation behaviour of the polymer network. We assert that is the unique physical structure of the low density CNT networks which provide a scaffold for the formation of inorganic silica on degradation - which is associated with a corresponding increase in bulk thermal stability. Such large and significant shifts in the degradation behaviour of a silicone based material as a result of the inclusion on a nano-material are highly novel and have not been reported previously. We feel on this basis, that the work presented here represents a significant contribution to the field of advanced composite materials degradation and stability.

It is our opinion therefore, that this work is sufficiently novel, relevant and fitting to warrant publication in Polymer Degradation and Stability, would be of general relevance and interest to the informed readership of your journal. We thank you for your consideration of this work.

Yours Faithfully,

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ABSTRACT

Carbon nanotube-carbon aerogel (CNT-CA) networks are a member of a novel class of ultra-low density, high surface area, hierarchically structured, carbon-based materials possessing unique mechanical and physical properties. Through the secondary incorporation of a polymer matrix into these aerogel systems it is now possible to form intercalated polymeric hybrid CNT-CA composite materials with polymer to carbon surface internal surface contact areas in the order of $\sim 600 \text{ m}^2 \text{ g}^{-1}$ at carbon loadings as low as $\sim 1.5 \text{ wt } \%$. Reported here is the synthesis of a series of well-defined poly(dimethylsiloxane) (PDMS)/CNT-CA composite systems, their characterization and the in-depth

analysis of the effects of the carbon architecture on the thermal stability and degradation behaviour of the of the PDMS matrix. The results of degradative thermal analysis using both pyrolysis gas-chromatography/mass spectrometry (py-GC/MS) and thermogravimetric analysis (TGA), clearly demonstrate that the presence of the CNT-CA scaffold within the PDMS matrix greatly increases the thermal stability of the system and drives the matrix towards calcination at temperatures above 600°C. Subsequent characterization of the residual materials using a combination of fast magic angle spinning solid-state nuclear magnetic resonance (Fast-MAS NMR), energy dispersive X-ray spectroscopy (EDAX) and electron microscopy have demonstrated that the improvements in thermal stability are concurrent with the relative loading of carbon nanotubes within the aerogel matrix, that the PDMS matrix is being driven towards the formation of increased levels of SiO₂ on degradation and that the preferential calcination effect is a function of the unique high surface area fibular network structure of the CNT-CA monoliths.

KEYWORDS: PDMS; Carbon Aerogels; Carbon Nanotubes; Hybrid Polymer Composites; NMR; Thermal Degradation; Pyrolysis

1. INTRODUCTION

Carbon nanotubes possess a number of intrinsic properties that make them potentially, highly desirable as filler materials and physical property modifiers in the design of the next generation of polymeric composites and hybrid materials. CNTs can have electrical conductivities as high as $1 \times 10^6 \text{ S m}^{-1}$ [1], thermal conductivities as high as $3000 \text{ W m}^{-1} \text{ K}^{-1}$ [2], elastic moduli of the order of 1 TPa [3], and are extremely flexible [4]. Unfortunately, the realization of these properties in macroscopic forms, such as in practical advanced polymer/CNT composites, has been limited due to the inherent problems associated with the effective, uniform dispersion of CNTs as a heterogeneous 2nd phase within a polymer matrix [5-7]. An alternative to the dispersion approach for the design of new composite systems that was originally suggested by Chen *et. al* in 2006 [8] and was more recently demonstrated by

the authors [9], is the use of a low-density, CNT/aerogel foam as a scaffold that can be intercalated by the polymer matrix.

We have extensive expertise in the synthesis and development of such ultralow-density CNT-based aerogel foams (CNT-CAs) and have reported the exceptional electrical and mechanical properties of this unique class of materials [10, 11]. In these nano-foams systems, carbon nanoparticles are used as a binder to crosslink randomly oriented bundles of single-walled CNTs. These CNT-CAs have been shown to simultaneously exhibit increased stiffness and high electrical conductivity even at densities approaching $1 \times 10^{-2} \text{ g cm}^{-3}$ [10]. The CNT-CA materials synthesized have also been shown to be highly thermally stable, maintaining their structural architecture and integrity (under non-oxidative conditions) up to temperatures approaching 1600°C and have been shown to be unaltered by exposure to extremely low temperatures during immersion in cryogenic liquids [12]. More recently the authors have also reported the synthesis of the first CNT-CA polymer composites using a commercial platinum-cured two part silicone resin (Dow Corning Sylgard 184) as the polymer matrix. The resultant composite system was shown to exhibit electrical conductivities over 1 S cm^{-1} and a 300% increase in the elastic modulus with as little as 1 vol% nanotube content [9].

Despite this progress in the synthesis of CNT-CA-polymer composite materials, the characterization of their chemical and physical properties has been somewhat hampered by the limitations of the commercial elastomer formulations used as the polymer matrix and have focused only on the measurement of the composite systems electrical conductivities / bulk mechanical properties [9]. To date, there have been no published data on the thermal stability and degradation behaviour of these systems - as the complex, highly filled and poorly described structure of the commercial silicone formations utilized [13] have complicated the interpretation of any thermal/chemical stability measurements or investigations of motional dynamics and relaxation behaviour.

However, through the use of a simple, structurally well-defined model polymer matrix, many of these complications which limit the mechanistic investigation of these important and novel systems may be removed.

It is well established that poly(siloxanes) thermally degrade above their ceiling temperature (c.f. linear PDMS: 110 °C) primarily via terminal and internal chain backbiting reactions [14-17] to yield a distribution of cyclic monomers, where the hexamethylcyclotrisiloxane or 'D₃' cyclic monomer is the thermodynamic and therefore most abundant product. It is well known that the thermal stability of polysiloxanes are sensitive to the presence of Lewis acids/bases [17, 18] and organo-metallic catalysts [19]. Additionally, the overall degradation pathways of polysiloxanes have been shown to be remarkably resistant to change due to additives, filler materials, catalyst residues or other contaminants [20]. Broadly speaking, a polysiloxane will always thermally degrade above its ceiling temperature to yield 30-80% of the D₃ cyclic and tailing distribution of higher cyclics from D₄ to D₂₀₋₃₀. This overall mechanism is well established and well understood [17, 21, 22]. Significantly less is known, however, about the effects of more exotic additives, fillers and heterogeneous secondary phases on the physical and chemical mechanisms of silicone degradation. Indeed, the authors have shown that poly(dimethylsiloxane) (PDMS) elastomers which physically incorporate nano-scale fillers, while still forming the D₃ cyclic as the major product of degradation, have a significantly altered profile of *minor* degradation products [23]. Additionally we have recently shown that aspects of a silicone network structures (network modality, number of free chain ends, cross-link density etc.) can quantifiably alter the statistical distributions of higher cyclic degradation products [24].

In this work we report the synthesis of a series of PDMS/CNT-CA composites through the use of a well-defined model end-linked PDMS network elastomer as the polymer matrix for CNT-CA nanofoams. The thermal stability and mechanistic thermal degradation behaviour of a series of PDMS/CNT-CA composites have been studied through the use of TGA, py-GC/MS, solid-state NMR EDAX and SEM. By using a simple PDMS network of known structure, we can report for the first time and without obfuscation, an in-depth study of the thermal degradation behaviour of these unique composite materials.

2. EXPERIMENTAL

2.1 Materials. All reagents were used without further purification. Resorcinol (99%) and formaldehyde (37% in water) were purchased from Aldrich Chemical Co. Sodium carbonate (anhydrous) was purchased from J.T. Baker Chemical Co. Highly purified CNTs were purchased from Carbon Solutions, Inc. Vinyl terminated PDMS of average molar mass 28 Kg mol⁻¹, Poly(methylhydrosilane) of average molar mass 2.45 Kg mol⁻¹, tetravinyl-tetramethylcyclo-tetrasiloxane and a platinum-cyclovinyldimethylsiloxane complex were all purchased from Gelest Inc.

2.2 Preparation of CNT-CA nanofoams. Nanofoams were prepared using traditional organic sol-gel chemistry. [25] In a typical reaction, purified CNTs (Carbon Solutions, Inc.) were suspended in deionized water and thoroughly dispersed using a VWR Scientific Model 75T Aquasonic sonication bath (sonic power ~ 90 W, frequency ~40 kHz). The concentration of CNTs in the reaction mixture ranged from 0 wt% to 1.3 wt%. To determine the optimal conditions for CNT dispersion, a range of sonication times (4 to 24 hrs) were evaluated. Once the CNTs were dispersed, resorcinol (1.235 g, 5.6 mmol), formaldehyde (1.791 g, 11.1 mmol), and sodium carbonate catalyst (5.95 mg, 0.028 mmol) were added to the reaction solution. The resorcinol to catalyst ratio (R/C) employed for the synthesis of the composites was 200. The sol-gel mixture was then transferred to glass moulds, sealed and cured in an oven at 85°C for 72 h. The resulting gels were then removed from the moulds and washed with acetone for 72 h to remove water from the pores of the gel network. The wet gels were subsequently dried with supercritical CO₂ and pyrolyzed at 1050°C under a N₂ atmosphere for 3 h. The composite materials were isolated as black cylindrical monoliths. Foams with CNT loadings ranging from 0 to ~80 wt% were prepared by this method. For comparison purposes, pristine carbon aerogels without CNTs were also prepared using the method described above without the addition of CNTs.

2.2 Preparation of PDMS/CNT-CA composites. For the purpose of this study, an end-linked, hybrid tetra/comb crosslinked ‘model’ network was developed that formed via a platinum mediated vinyl addition reaction between vinyl terminated poly(dimethylsiloxane) (PDMS), 2 Wt. % tetravinyl-tetramethylcyclo-tetrasiloxane (which acts as a cure rate moderator) and a stoichiometric level of an

oligomeric poly(methylhydrosilane). This network formulation was designed to have an initially low starting viscosity, a pot-life of ~4 days at room temperature and a high final crosslink density. These properties make it an ideal material for controlled intercalation into the CNT-CA monoliths.

In order to prepare a PDMS/CNT-CA composite system, 9.8 grams of vinyl terminated PDMS and 0.2g of tetravinyl-tetramethylcyclo-tetrasiloxane were combined with a stoichiometric level of poly(methylhydrosilane) crosslinker in the presence of 10 ppm of a Pt cyclovinyldimethylsiloxane complex and mixed for 30 seconds using a Flacktektm Speedmixer off-axis centrifugal mixer at a rate of 2500 rpm. The mixed resin was then cooled in an ice-bath to a temperature of 5°C. A CNT-CA monolith was immersed fully into the cooled resin and placed under vacuum for 2 hours at 5°C to begin the process of exchanging the air in the monolith with the resin mixture. When bubbling was observed to cease from the monolith in the resin bath, the sample was brought up to atmospheric pressure, agitated gently and returned to vacuum. Five such cycles were repeated to ensure that the polymer resin had fully penetrated the nanofoam matrix. Once the intercalation stage was completed, the resin containing the CNT-CA monolith was brought up to a temperature of 50°C and allowed to cure for 24 hours to form a solid elastomeric block. The cured, intercalated monolith was subsequently cut from the elastomer using a scalpel and each recovered cylinder of PDMS/CNT-CA composite was sectioned longitudinally to ensure that the intercalation of the polymer into the matrix was complete and homogeneous. In this manner, a total of six PDMS/CNT-CA composite systems were synthesized with CNT loadings ranging from 0-80 wt. % relative to CA. In addition, a sample of non-intercalated PDMS network was also synthesized for control and comparison purposes. Given in **Table 1** is a summary of the systems prepared for this study.

[Table 1]

2.3 Thermogravimetric Analysis. Analyses were carried out using a Perkin Elmer TGA-7. Samples (~25 mg) of each model elastomer were heated at 10 °C /min under a purge flow of nitrogen from 25 to 800 °C. These data obtained were plotted in the form of 1st derivative Δ mass vs. temperature. Onset and peak degradation temperatures were extracted from these curves.

2.4 Analytical Pyrolysis. All pyrolysis studies were carried out using a CDS Analytical 5150 Pyro-probe coupled to an Agilent 7890 GC with an Agilent 5973N quadrupole MSD for detection of analytes. Samples (~50 µg) of each prepared composite were massed into quartz sample tubes. The sample tubes were loaded into the Pt filament coil of the pyro-probe apparatus for pyrolysis. The sample was held at an initial temperature of 60°C for 0.5 min, and then pyrolysed at a ballistic heating rate from 60 to 1000 °C under a purge flow of helium for a total pyrolysis time of 2.0 min. The pyrolysates were continually transferred from the pyro-probe apparatus to the GC inlet using an inert transfer line (both at 300 °C) with a 20:1 split flow for the total pyrolysis runtime. An HP-5 (30 m x 0.25 mm i.d. x 0.25 µm i.f.) analytical column under constant flow of 3.0 ml/min with Helium carrier gas was used. The initial GC oven temperature was set at 40°C for 2.0 min and then ramped at 10 °C /min to 300 °C and held for 10 min at the final temperature for a total analysis time of 38.0 min. The MS ion source and quadrupole were 230°C and 150°C, respectively. Total ion chromatograms (TIC) of the pyrolysis products were collected for each run. Five replicate analyses were carried out for each sample.

2.5 Equilibrium solvent uptake measurements. Solvent swelling of the samples was performed using a 5:6 v/v toluene/acetone mixture at 29.5 °C as the swelling medium which provides theta conditions for the polymer chains. Samples of ~25 mg mass were swollen under these conditions for 48 hours and triplicate samples of each system were swollen for statistical accuracy. The swollen samples were surface dried then weighed using a sensitive microbalance (Mettler Toledo) to an accuracy of $\pm 5 \times 10^{-7}$ grams. After measurement, the networks were un-swollen gradually in methanol then dried in a vacuum oven overnight at 45 °C. The samples were weighed again and these values were used to calculate the fraction of soluble material extracted during the swelling process.

2.6 Fast-MAS ^{29}Si NMR. Solid-state ^{29}Si single-pulse magic angle spinning nuclear magnetic resonance (SP/MAS NMR) spectra were collected on a 600 MHz Bruker Avance III spectrometer using a Bruker Very Fast MAS probe configured for 1.3 mm (o.d.) rotors. Samples were spun at 40 kHz, and the spectrum collected using a 6 µs excitation pulse with a 2 s recycle delay for all acquisitions. This

pulse length and acquisition delay were used to optimize the amount of time required to collect a spectrum with reasonable signal to noise. The spectrum was referenced with respect to tetramethylsilane (0 ppm).

2.7 SEM and EDX analysis. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) characterization were performed on a JEOL 7401-F at 5-10 keV (20mA) in SEI mode with a working distance of 2-8 mm.

3. RESULTS AND DISCUSSION

3.1 Initial physical characterization of the PDMS/CNT-CA composite systems. - Equilibrium solvent uptake and SEM analysis. Beyond the basic visual assessment of the homogeneity of the intercalation and the completeness of silicone curing reaction, efforts were made to determine the level of interaction between the polymer matrix and CNT-CA foam through both solvent swelling measurements and electron microscopy. Shown in **Figure 1** are the results of equilibrium solvent uptake analysis of the base elastomer and the 6 composite systems. Measured solvent swelling ratios were used to derive values of an effective inter-crosslink chain length through the use of the Flory Huggins relationship [26].

[Figure 1]

From the data shown in **Figure 1** it can be observed that the fully cured base silicone network has an effective inter-crosslink chain length of $\sim 14000 \text{ g mol}^{-1}$ which is consistent with a network based on a 28000 g mol^{-1} PDMS with a poly-functional cross-link chemistry. The composite systems in contrast show on average, a reduction in inter-crosslink chain length of $\sim 10000 \text{ g mol}^{-1}$. This suggests that there is a strong interaction between the PDMS chains and the CNT-CA foam structure. While this is thought to be a purely physical interaction, the magnitude of the decrease in network swelling suggests that the polymer-carbon interaction is at least as strong as those typically observed between PDMS and high surface area, fumed silica [27-29]. What is also apparent from the data is that the level of polymer-composite interaction is not strongly influenced by the level of CNT's present in the nanofoam. Further confirmation of the intimate association between the polymer and carbon matrixes has been provided

though SEM imaging of freeze fracture samples of the formulated composites. Shown in **Figure 2** is one such SEM image of a freeze fracture surface of the 20/2 PDMS/CNT-CA composite material.

[Figure 2]

3.1 Determination of the thermal stability of the composite systems. Thermogravimetric and pyrolytic analysis. Both non-oxidative TGA and analytical pyrolysis were utilized to determine the thermal stability of the composite systems and investigate the effects of the carbon matrix on the degradation of the silicone network. TGA of relatively large samples ~25 mg at 10°C/min yields information on the degradation of the composite systems in a diffusion limited regime whereas micro-analytical pyrolysis (~0.05mg at 100°C/min) allows the degradation process(s) to be studied under more ideal non-diffusion limited conditions [13, 30]. Shown in **Figures 3 & 4** are the collected TGA and analytical pyrolysis thermograms from the non-oxidative degradation of all the systems studied. Onset, peak evolution data and % volatiles evolution data are given for these analyses in **Table 2**.

[Figure 3]

[Figure 4]

[Table 2]

It can be observed from **Figures 3 & 4** that the base elastomer has a degradation profile typical of an end-linked PDMS based network [13, 17, 20, 24], having an onset of ~500°C, a two stage degradation profile, consistent with de-polymerization and cyclization processes followed by secondary high temperature radical scission reactions and a degree of calcination. What is also apparent from these data is that the incorporation of the 0/2 carbon aerogel foam into the silicone elastomer drastically decreases its thermal stability and alters its degradation profile: The elastomer is observed to degrade in a single stage process and in a non-diffusion limited regime the onset of degradation was observed to decrease by ~ 55°C. And this major change in the degradation behaviour appears to be entirely a consequence of the presence of the aerogel matrix. Just as significant however, is effect of increasing levels of CNT's in the composite systems. With increasing weight fraction of CNT's in the foams, the thermal stability of the PDMS/CNT-CA composites increase and at an 80% wt. fraction of CNT's relative to CA, (sample

20/2) in a non-diffusion limited degradation process, the onset of thermal degradation increased by ~100°C compared to the base elastomer. These trends are summarized in **Figure 5**.

[Figure 5]

The levels of volatile degradation products produced may also be assessed for both the diffusion limited and non-diffusion limited cases. Shown in **Figure 6** are the trends in total volatiles released from both the TGA and pyrolysis data.

[Figure 6]

It is clear from the trend data in **Figure 6** that in both the diffusion limited ‘bulk’ (TGA) and a non-diffusion limited regime (Py-GC/MS) degradation regime, that the PDMS/CA composite material evolves increased levels of volatiles with respect to the unfilled base elastomer. It is also very clear from these data that as the level of SWNT are increased in the composites, the level of volatile matter evolved from the systems decreases as a function of nanotube loading.

It is evident from these data that the presence of a CNT-CA foam matrix in a PDMS elastomer has a profound effect on the thermal degradation behaviour of the polymer network. And while a CA foam matrix negatively impacts the thermal stability of the PDMS matrix, CNT-CA foams in fact impart significant increases in thermal stability; significantly alter the rate of degradation and the levels of volatiles released. In section 3.2 the mechanistic origins of these marked changes in degradation behaviour are discussed.

3.2 Chemical speciation of degradation products and analysis of char residues. In addition to obtaining pyrolysis thermograms, the Py-GC/MS studies were repeated for each sample using the GC column in an eluting mode. As such, the pyrolysates from the degradation of each system were separated and speciated. Shown in **Figure 7** is a composite TIC plot showing the speciation of major and minor degradation products for all systems studied.

[Figure 7]

The analysis of the degradation products given in **Figure 7** not only confirms that the base silicone elastomer degrades via the established mechanism of cyclization to form cyclic oligomers (with the

thermodynamic 'D₃' product being the most plentiful), it demonstrates that major degradation mechanism pathways are broadly unaffected by the presence of the secondary carbon network in the silicone matrix. These observations would appear to support the hypothesis that the increases in thermal stability are the result of a physical mechanism and not a change in the degradation chemistry of the silicone network. It is also worthy of note that the 0/2 (PDMS/CA composite) which has exhibited decreased thermal stability and increased levels of volatiles evolution, compared with the base elastomer, was shown to have small yet significant levels of branched and linear siloxanes species which are indicative of radical degradation processes [31] and suggest that the CA matrix in this composite may be promoting scission reactions in the siloxane network which lead to the observed decreases in matrix stability.

Analyses of the intractable char residues from the degradation of the composite systems were conducted using a combination of SEM, EDX and solid state NMR. SEM images of various PDMS/CNT-CA char residues are given in **Figure 8**. Note that no significant char residue was obtained from the base elastomer.

[Figure 8]

The SEM analysis indicates that in all cases the nanofoam matrix remains intact even after pyrolysis and that the majority of the PDMS matrix has degraded and volatilized. However, in the CNT-CA composite residues appears to be evidence of the deposition of a layer of a secondary calcined material which is visible on the surface of the nanotube network.

EDX analysis of the char residues was also carried out in order to determine the elemental composition of the chars examined by SEM. The only elements detected in any significant quantity in all samples were carbon, silicon and oxygen. The results of the EDX compositional analysis are given in **Table 3**.

[Table 3]

The results of the EDX elemental compositional analysis of the char residues given in **Table 3** clearly show that in general, the CNT-CA systems have a significantly higher silicon content than the CA nanofoam system and that the calcined layer observed in the SEM images is rich in silicon.

²⁹Si Solid state NMR analysis of the residues, the results of which are given in **Figure 9** - demonstrate that this calcined layer is predominantly inorganic SiO₂.

[Figure 9]

Solid state NMR analysis of selected char residues have demonstrated that the silicon found in these residues is in the form of amorphous silica which is most likely to have been formed from the condensation of the portions of the PDMS network on degradation. While a degree of silica formation on the pyrolytic degradation of silicone systems is not uncommon [17], the levels typically encountered on the non-oxidative degradation of an unfilled silicone network are less than 5 weight % in a given residue. The high levels of silica (~30-40 wt. % silicon from EDX) found in the residues of the CNT-CA/PDMS composites suggest that a marked change in the condensed-phase degradation mechanism of these systems has occurred when compared with the base elastomer and even the PDMS/CA composite system. From a simple mass balance perspective – we observe a decrease in the formation of volatile silicone oligomers on decomposition in the PDMS/CNT-CA composites associated with a corresponding increase in the levels of calcined silica formation. What is both interesting and significant however; is that it appears to be the CNT-CA nanofoam matrix that is the driving force for this preferential calcination on degradation. The unique high surface area, low density network of the carbon nanotubes bound by carbon aerogel particles would seem to be providing a physical scaffold for the formation of condensed silica from the silicone matrix and it is this shift towards calcination of the network which is the physical basis for the improved thermal stability of these composite systems.

4. CONCLUSIONS

The inclusion of an ultra-low density CNT-CA inorganic carbon framework into a cross-linked poly(dimethylsiloxane) network has a significant effect on the non-oxidative thermal stability and

condensed phase degradation behaviour of the polymer network. While the inclusion of a carbon aerogel matrix into a well-defined PDMS elastomer system has actually been shown to have a deleterious effect on the thermal stability of the composite system, lower density SWNT nanofoams bound with CA particles improve the thermal stability of the an intercalated PDMS matrix markedly. Analysis of both the evolved volatile degradation products and the condensed-phase char residues of such PDMS/CNT-CA hybrid composites clearly demonstrates that while distribution of volatile oligomeric degradation products remains broadly unaffected by the presence of the CNT matrix, the yield of volatile cyclic oligomers decreases in favour of the formation of calcined silica on the surface of the intact nanotube matrix. Our analyses show clearly that the unique physical structure of the low density CNT networks provide a scaffold for the formation of inorganic silica on degradation - which is associated with a corresponding increase in bulk thermal stability. Such large and significant shifts in the degradation behaviour of a silicone based material as a result of the inclusion on a nano-material are highly novel and have not been reported previously. It is the aim of the authors to continue to study these interesting effects in greater depth using a combination of degradative thermal analysis and NMR methodologies to better define the relationship between the motional dynamics and stability of the polymer matrix in relation to carbon nanotube networks and other frameworks.

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TABLES

Table 1. Summary of the formulated composite systems.

Composite system	Sample identifier	CNT-CA foam wt. % relative to silicone	Wt. % CNT relative to CA	Density of CNT-CA foam (gcm ⁻³)
Base silicone elastomer	Base	N/A	N/A	N/A
PDMS/CA	0/2	11	0	0.105
PDMS/CNT-CA	1/2	9	4	0.089
PDMS/CNT-CA	2/2	7	8	0.070
PDMS/CNT-CA	5/2	5	20	0.051
PDMS/CNT-CA	10/2	3	39	0.027
PDMS/CNT-CA	20/2	2	78	0.015

Table 2. Tabulated values of onset, peak degradation and total mass loss/volatile evolution data from the TGA and pyrolytic degradative analyses of the PDMS/CNT-CA sample matrix.

System	Onset temp. /°C (TGA)	Onset temp. /°C (Pyro.)	Peak loss rate temp. /°C (TGA)	Peak loss rate temp. /°C (Pyro.)	% mass loss (TGA)	Total volatiles evolved (Pyro.) x10 ⁸ area counts/mg
Base	508 ± 3	517 ± 3	566 ± 3	607 ± 3	78.73 ± 0.01	2.0

0/2	487 ± 3	462 ± 3	523 ± 3	539 ± 3	88.67 ± 0.01	2.2
1/2	514 ± 3	614 ± 3	618 ± 3	720 ± 3	83.64 ± 0.01	1.5
2/2	488 ± 3	547 ± 3	546 ± 3	648 ± 3	84.35 ± 0.01	1.2
5/2	521 ± 3	551 ± 3	632 ± 3	655 ± 3	82.49 ± 0.01	1.3
10/2	536 ± 3	564 ± 3	627 ± 3	685 ± 3	82.67 ± 0.01	1.2
20/2	540 ± 3	614 ± 3	634 ± 3	814 ± 3	80.72 ± 0.01	0.9

Table 3. EDX elemental compositional analysis of the char residues obtained from pyrolysis of the composite materials studied. Note that for all samples, only carbon, oxygen and silicon were observed in any significant quantity.

Composite char	Wt. % Carbon	Wt. % Oxygen	Wt. % Silicon
0/2	74.03	17.31	8.66
1/2	61.08	29.49	9.33
2/2	51.70	33.73	26.07
5/2	28.84	28.26	42.90
10/2	28.87	35.80	35.34
20/2	41.25	36.41	22.35

FIGURE CAPTIONS

Figure 1. Derived effective inter-crosslink chain length for the base elastomer and each CNT-CA system. It is observed that in the composite materials, the effective distance between network ‘anchoring points’ has diminished markedly.

Figure 2. SEM image of a freeze fracture surface of composite 20/2. The bulk of the material is of course the PDMS matrix, however wire-like CNT/CA structures are observed throughout the polymer and appear to be ‘coated’ in many cases with the polymer matrix.

Figure 3. Composite 1st derivative TGA thermograms showing the mass loss as a function of temperature for 25 mg samples of each composite system. A-G Correspond to the base-20/2 systems respectively. Note that the PDMS/CA composite system is actually significantly less thermally stable than the base silicone elastomer, however as the loadings of CNT’s are increased in the foam matrix, we observe large increases in thermal stability. Tabulated values corresponding to these trends can be found in **Table 2**

Figure 4. Composite Pyrolysis thermograms showing the relative levels of volatiles evolved as a function of temperature for 0.05 mg samples of each composite system, normalized to sample mass. A-G correspond to the base-20/2 systems respectively. As with the bulk degradation profiles obtained by TGA the PDMS/CA composite system is shown to be significantly less thermally stable than the base silicone elastomer and as loadings of CNT’s are increased in the foam matrix, we observe large increases in thermal stability and reductions in total levels of evolved volatile material. Tabulated values corresponding to these trends can be found in **Table 2**.

Figure 5. Onset degradation temperatures as determined from TGA and analytical micro-pyrolysis. In both a diffusion limited and non-diffusion limited degradation regime the carbon aerogel foam reduces the thermal stability of the polymer matrix but as the loadings of CNT's in the nano-foam are increased from 0-80 wt. % the thermal stability of the polymer matrix is observed to increase markedly.

Figure 6. Total volatiles released as determined from TGA and analytical micro-pyrolysis. In a diffusion limited regime, all of the composite systems evolve increased levels of volatiles compared with the base elastomer and the least thermally stable 0/2 (PDMS/CA composite) evolves as much as 10% more volatile material on degradation. In the non-diffusion limited regime the trend is very similar, with the exception that the base and 0/2 systems do not show such a large disparity in relative levels of volatiles released.

Figure 7. GC/MS Total ion chromatograms of the separated and speciated degradation products from the ballistic pyrolysis of all systems studied. A-G Correspond to the base-20/2 systems respectively. Significant peaks are labelled 1-7 and correspond to (1) air, (2) methane/CO₂, (3-7) D₃-D₇ cyclic siloxane oligomers where the D₃ cyclic is the most abundant in all cases. Note that the presence of a carbon or nanotube network does not appear to alter the speciation of degradation products significantly.

Figure 8. Composite SEM images of the char residue surfaces of a range of composite systems. Top left 0/2, top right 2/2, bottom left 5/2 and bottom right is the 20/2 residue. Note that the nanofoam structure remains intact after pyrolysis in all cases; however there appears to be a layer of secondary material coated onto the surface of the nanofoam structure which becomes more pronounced as the CNT loading is increased.

Figure 9. Solid State ²⁹Si MAS NMR spectrum of the 10/2 composite residue. A single species of silicon was detected with a chemical shift that corresponds to amorphous silica [32].

Figure 1
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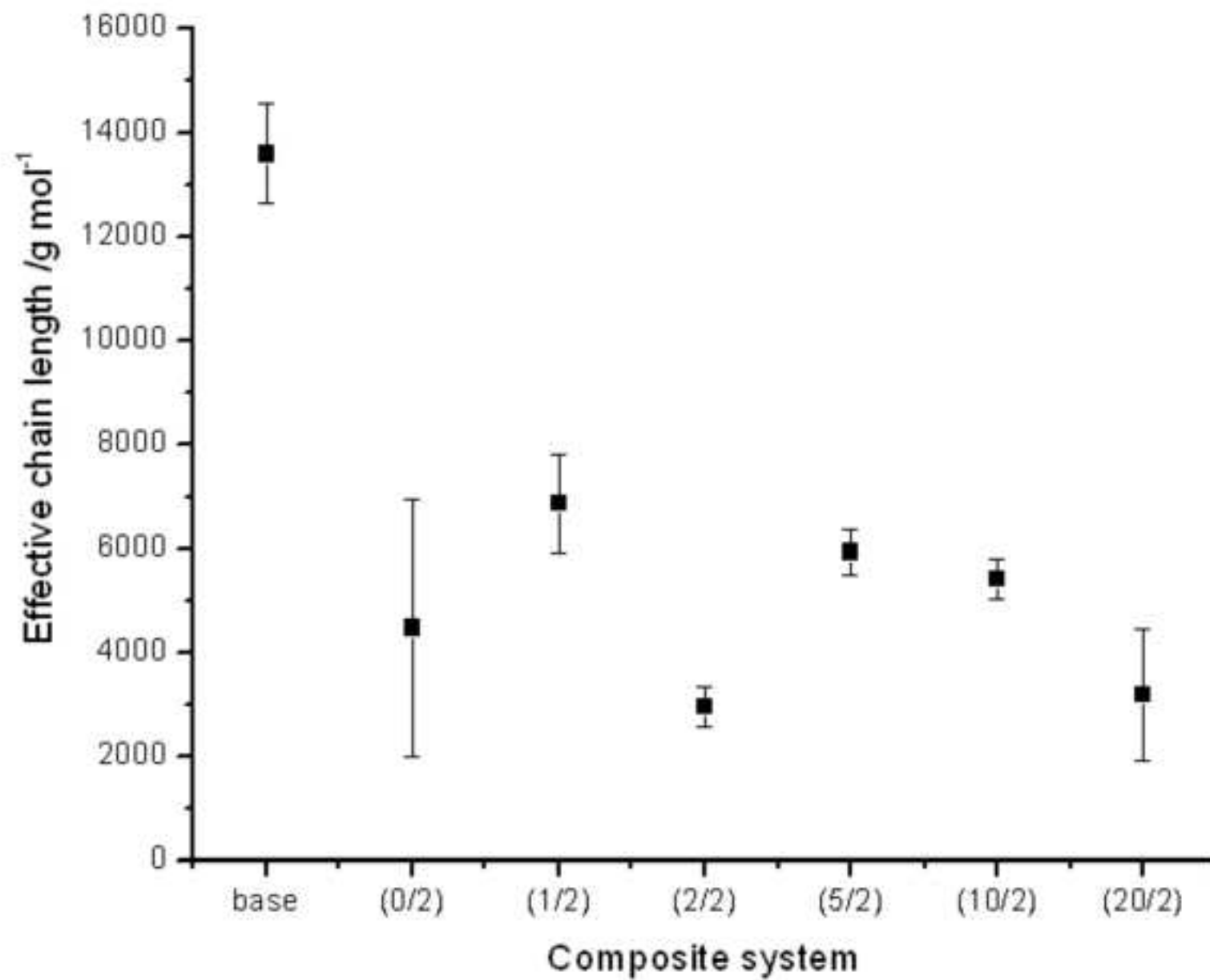


Figure 2
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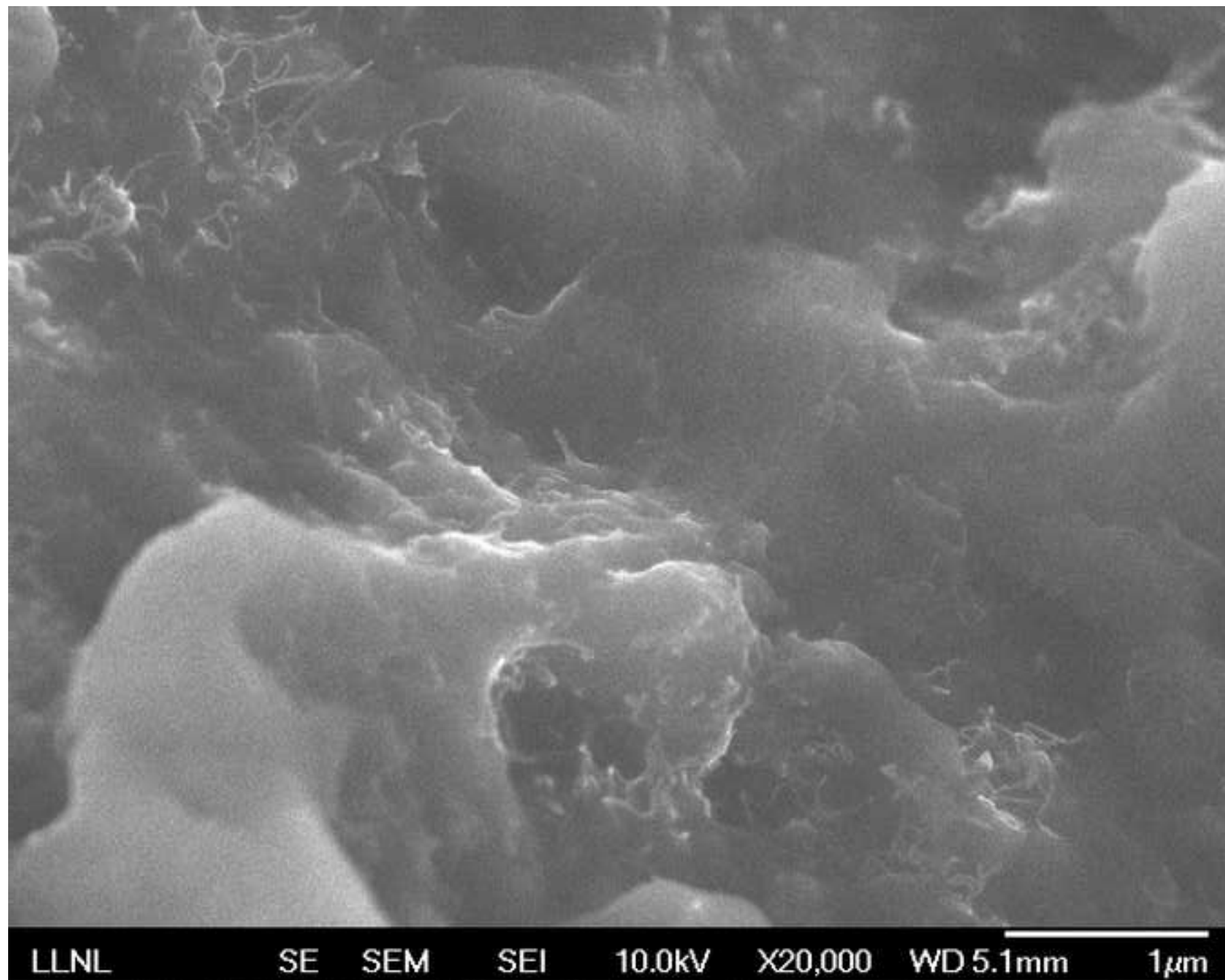


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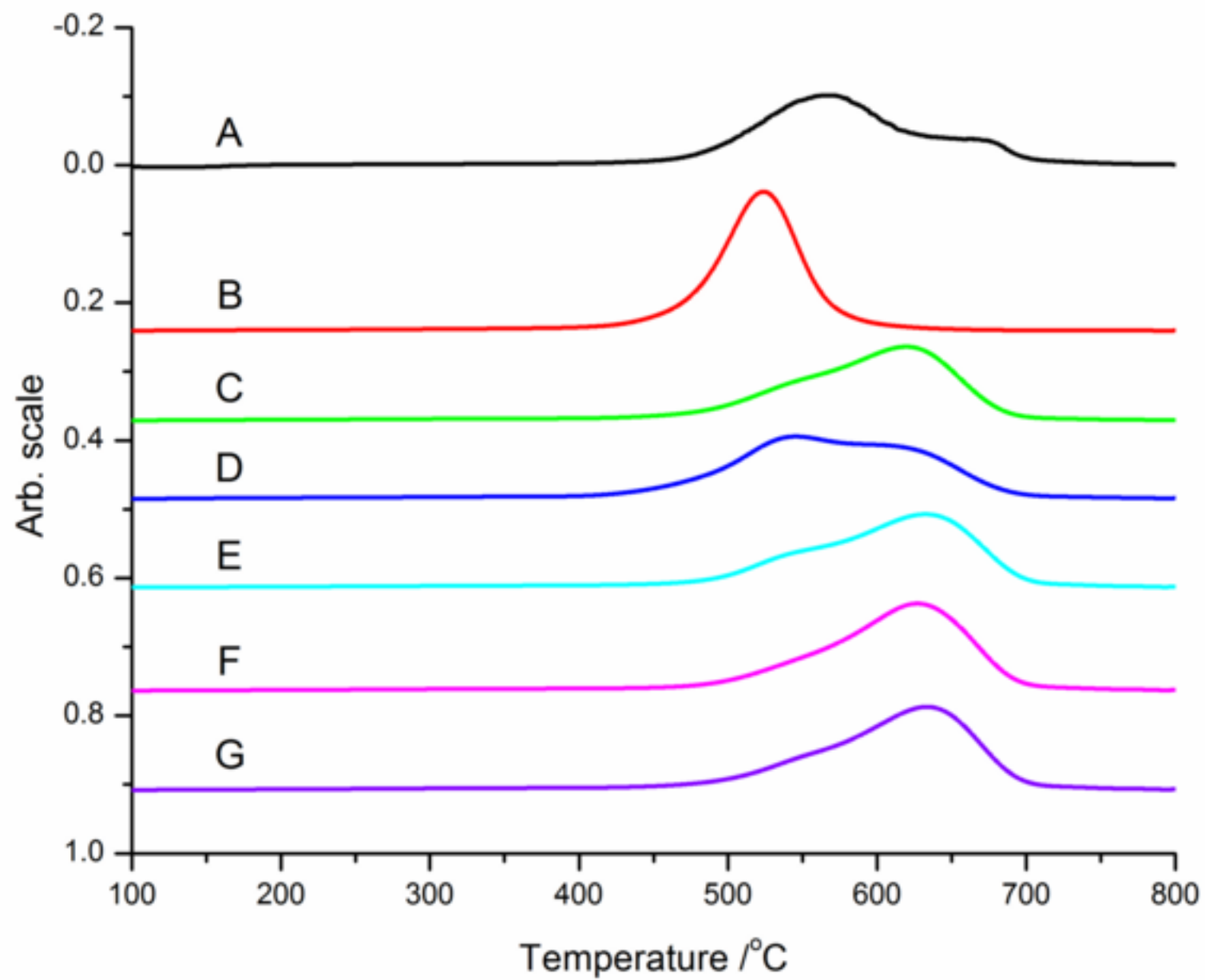


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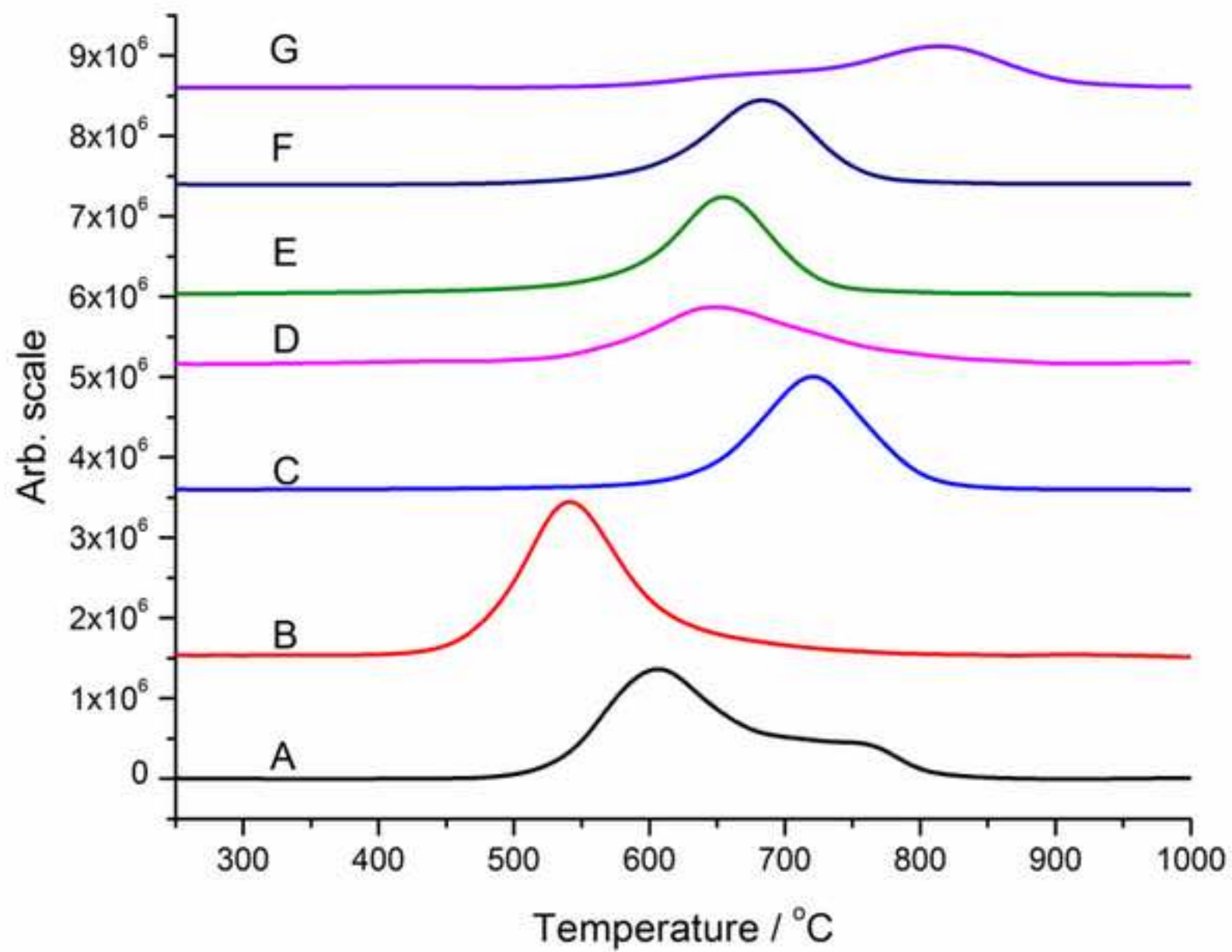


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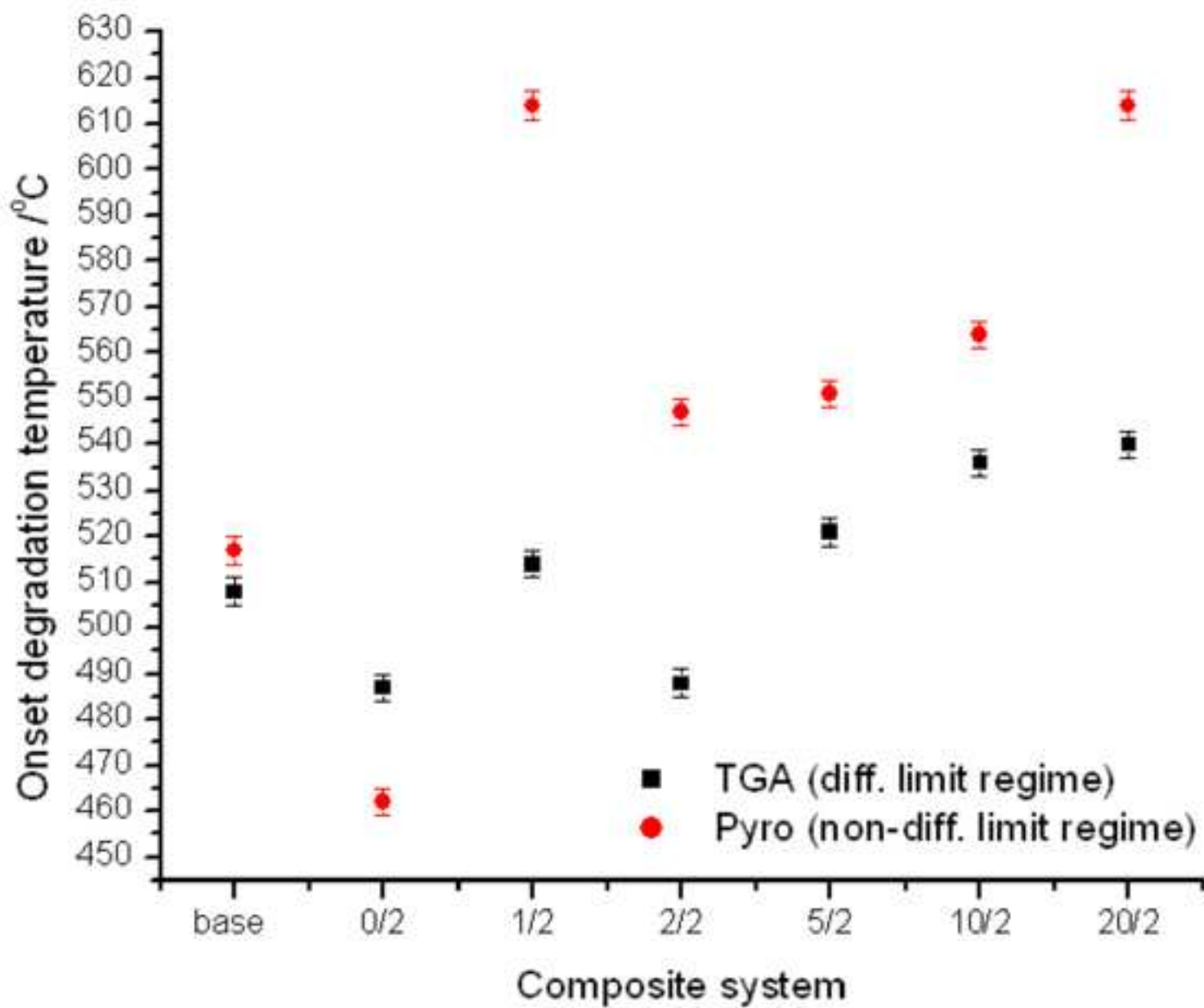


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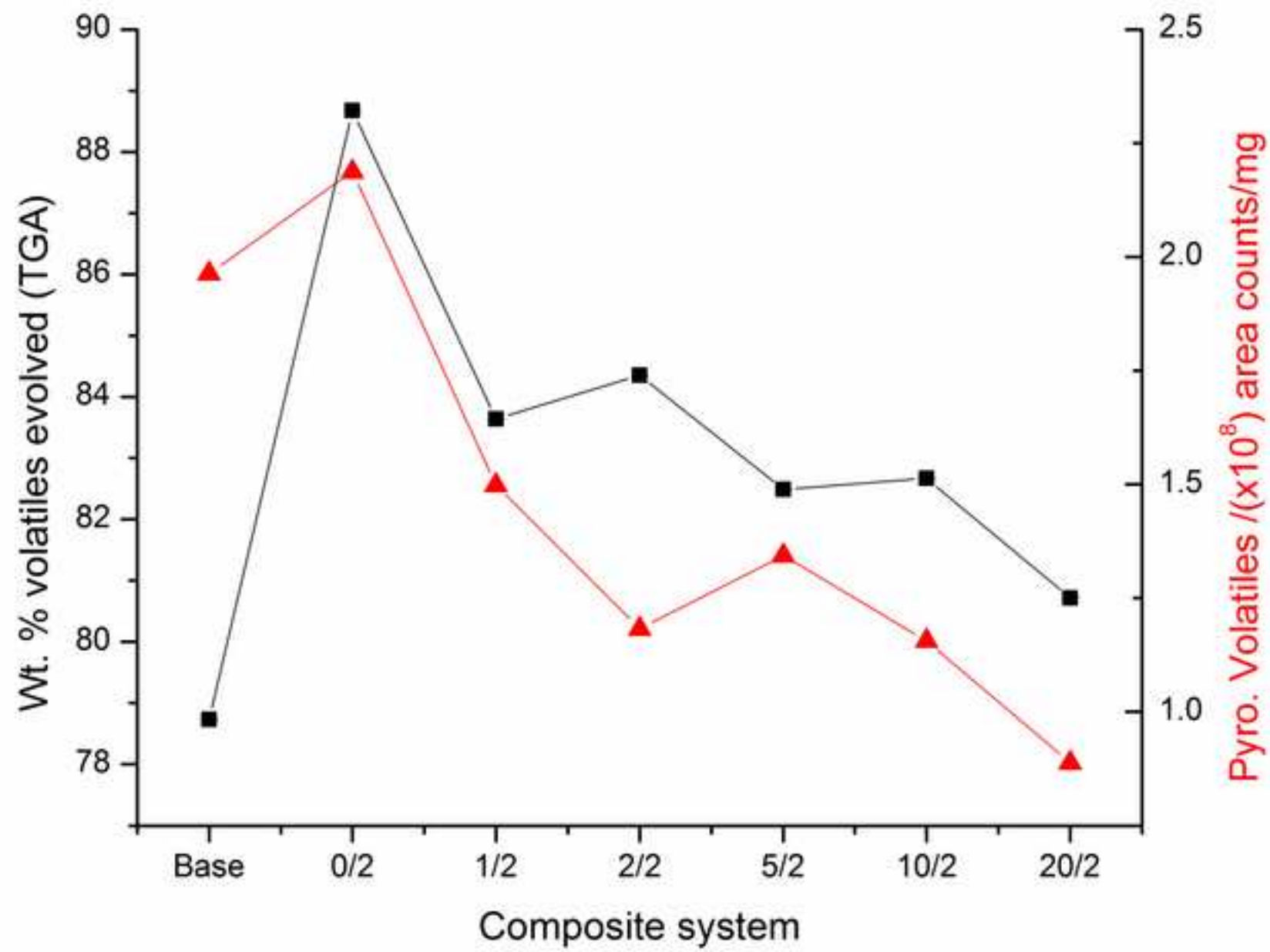


Figure 7
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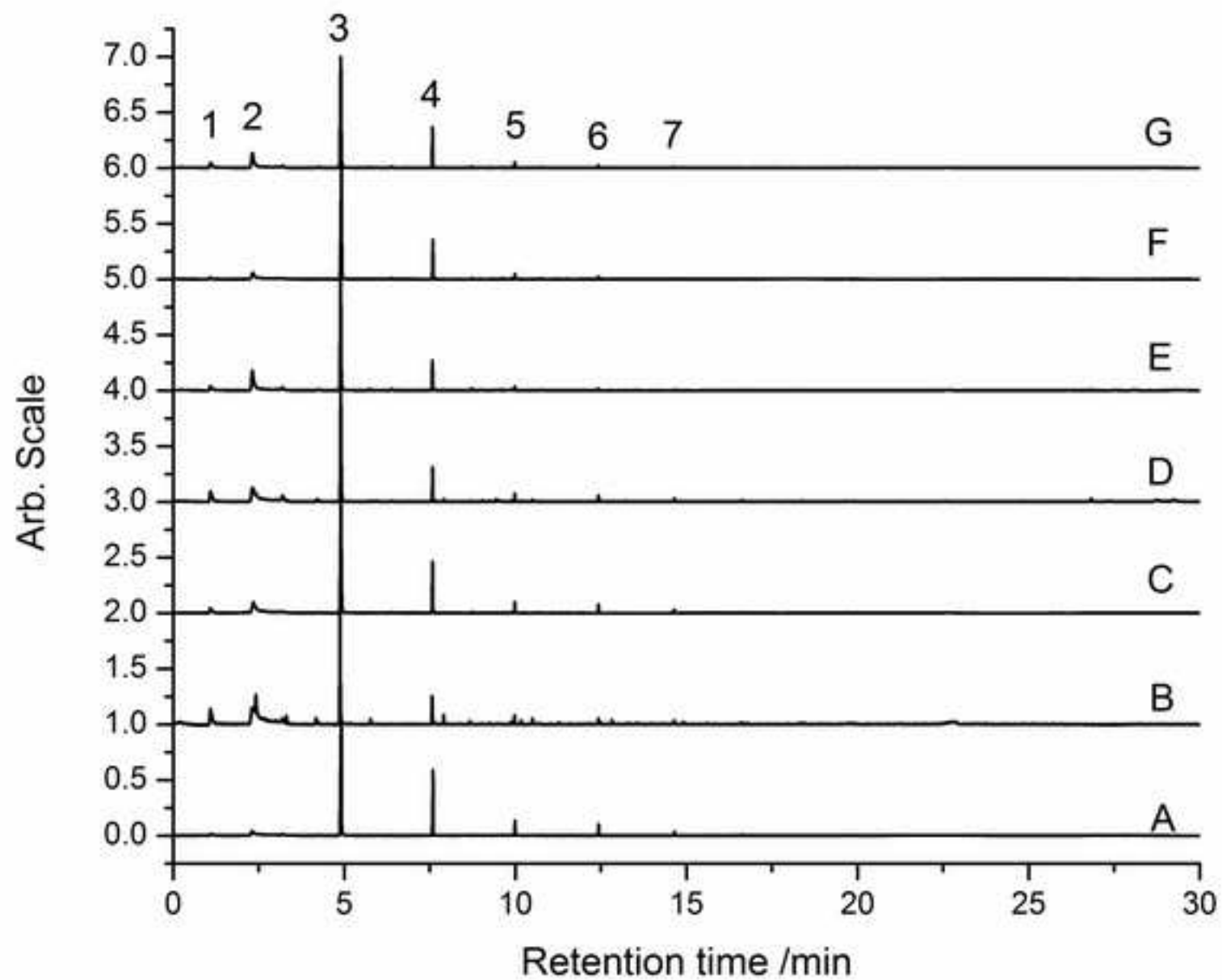


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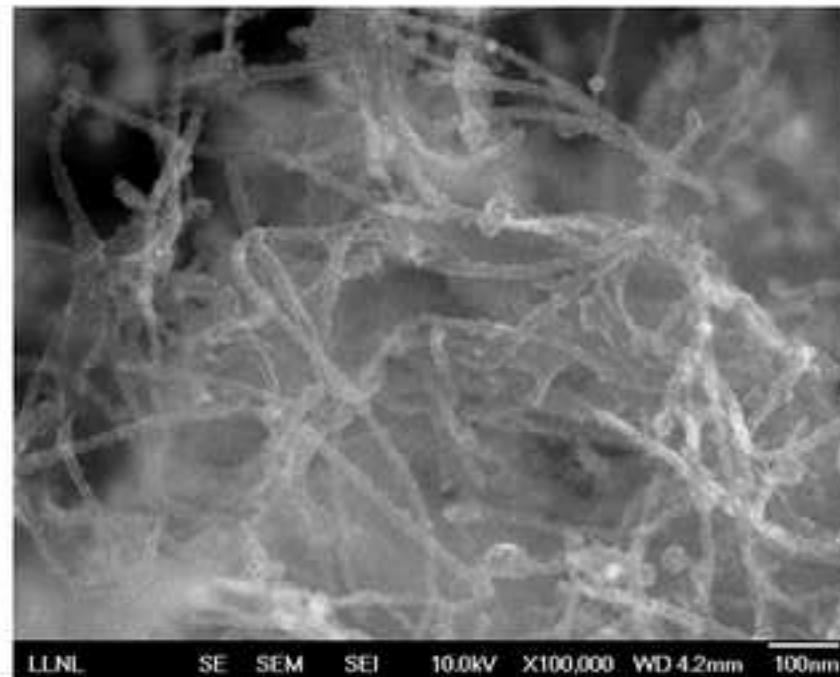
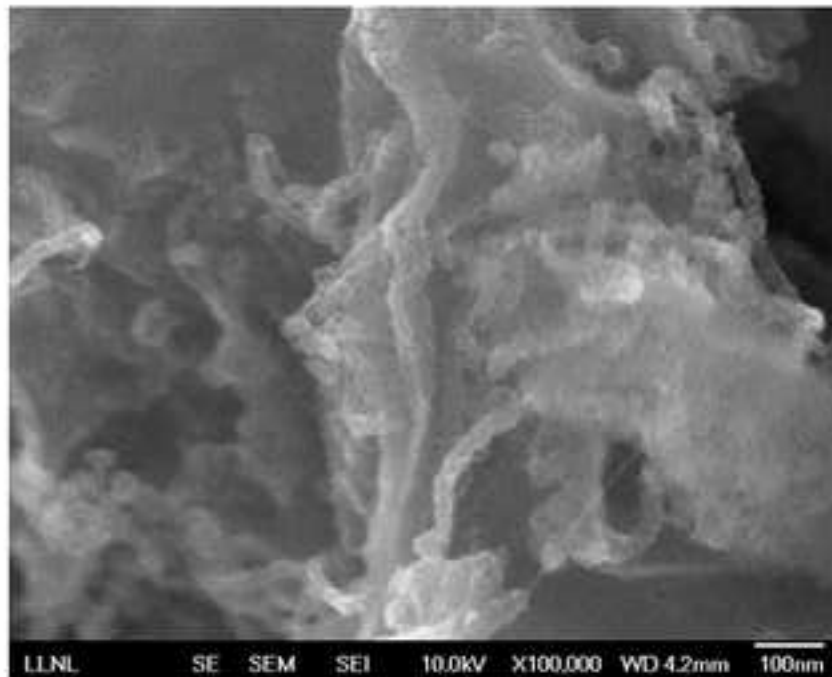
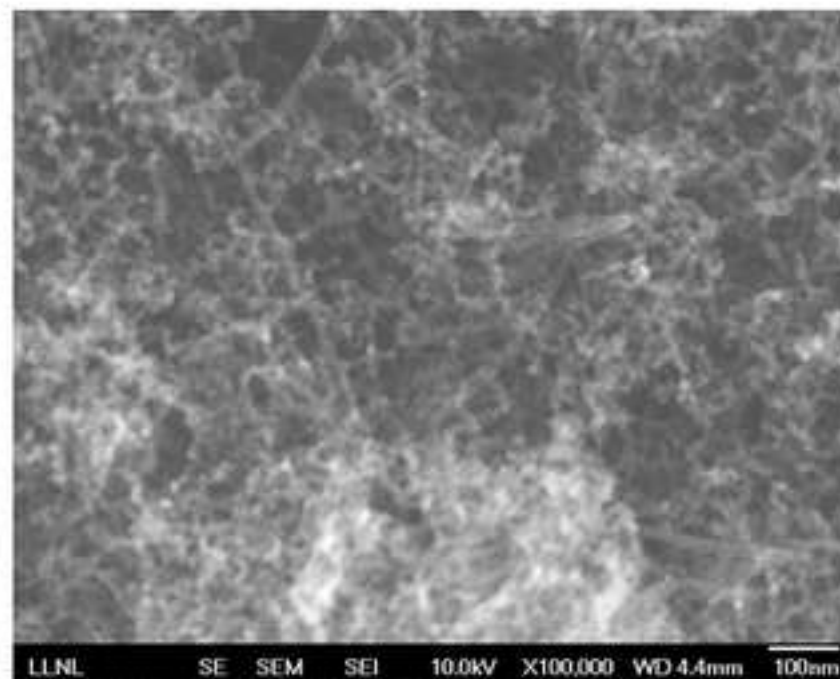
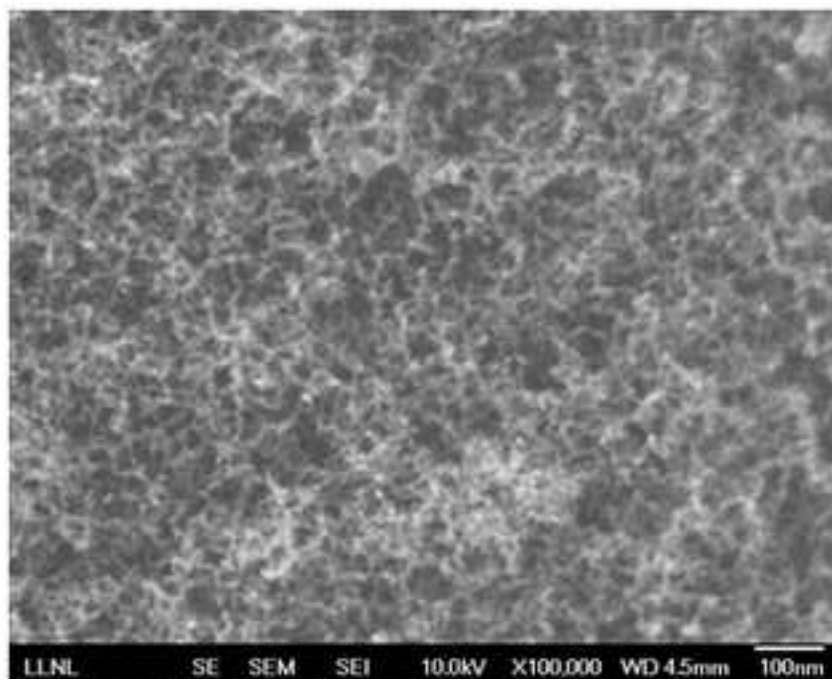


Figure 9
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